Indian J. Phys. 77A (2), 103–107 (2003)

AN INTERNATIONAL JOURNAL
IJP A

Band structure studies in solids using X-ray spectroscopy

B S Acharya
Regional Research Laboratory, Bhubaneswar-751 013, Orissa, India
E-mail : bs_acharya@yahoo.com

Abstract : The advent of X-ray photoelectron spectrometer and high energy synchroton sources have renewed interest in X-ray spectroscopical investigation of matter, be it solid, liquid or gases. Out of all spectroscopies available for study of electronic structure of material, X-ray spectroscopy has a spectacular contribution like optical spectroscopy and has enriched the knowledge of electronic structure of atoms, molecules and condensed matter. The analysis of X-ray transitions between atomic levels is a very direct method of studying atomic structure and experimental determination of X-ray energy lines give proof to the theoretical models. Thus the spectra from metals, semiconductors and insulators in the form of pure element, alloys and compound provide detail information about the density of states near Fermi level as well as those in the conduction and valence bands. Non-diagrams lines or the satellites provide a lot of information about the quasi states and vacancies between valence and conduction bands. Shift of X-ray emission and absorption lines provide information on the valence of the elements charge associated with it and the bonding present in alloys and compounds. In this short paper, usefulness of X-ray spectroscopic investigation on some metals, alloys, semiconducting thin films and insulating materials is highlighted. Study on these samples have shown the type of bonding present in alloy thin films, charge associated with different atoms, density of states present on the top of valence band and near the Fermi level. Further, the role of Coster-Kronig process of vacancy production, many electron effects and exchange interaction between *d* and *p* states are also discussed.

Keywords : Band structure, electronic states, X-ray fluorescence.

PACS Nos. : 78 70.En, 78.55.Et

1. Introduction

Twentyfirst century is going to see the challenges of real materials because of their complexity due to multi-atom effects and various defects in microscale/nanoscale during their synthesis or preparation. Both structure and chemistry have challenged the conventional method of structure determination and electronic properties. Nanostructural materials have thrown open the challenge for new characterization methods and hence there has been an upsurge in this direction to use methods like soft X-ray emission spectroscopy (SXS), extended X-ray absorption fine structure analysis (EXAFS), high resolution transmission electron microscopy (HRTEM), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) *etc.* Variety of probes used for characterization of nanostructured materials has been reviewed recently [1,2,3]. While the review of Redlich *et al* [2] emphasizes the complimentary use of electron and scanning probe microscopy as diagnostic tool to characterize nanomaterials. Yacoby *et al* [3] has used novel X-ray methods to obtain local atomic structure of materials. The concept of electronic structure of solids date back to 1930s. Angular momentum '*l*' which is a good quantum number in atoms or molecules is replaced by three dimensional crystal momentum vector by '*K*'. Consequently all electronic states in solids can be characterized by four quantum numbers $E(k)$. This relationship is generally referred to as band structure of solids. With the passing of time several analytical techniques like angle resolved photoelectron spectroscopy (ARPES), X-ray emission spectroscopy (XES) *etc.* have been developed as very powerful techniques to determine the electronic structure of solids. To confirm the theoretically predicted

band structures for new technologically important materials, electron interaction between individual atoms forming a solid or surface have to be understood in detail. While bulk electron interaction signifies electrical, thermal conductivities, magnetism, acoustic properties and mechanical stability, electronic structure of internal and external surfaces reflect properties like catalytic activities or corrosion of surfaces. Ultrathin surfaces and nanomaterials have been extensively used by researchers to study the quantum well states, surface states involved in Schottky barrier formation and adsorbed surface states for complex catalytic properties.

Soft X-ray emission (SXE), a process whereby a valence electron recombines with a vacancy in an outer core orbital in a radiative transition, has been used as a spectroscopic tool to study the electronic structure of atoms, molecules and solids. Although for some time it was replaced with photoelectron spectroscopy but with the advent of high energy photon source like synchroton, soft X-ray emission spectroscopy (SXES) has again come into prominance with more and more work being reported year after year [4]. Further, with the advent of high energy X-ray source, SXES have been used to study the electronic structure of compounds in greater details [5–10]. Recently there has been a renewed interest in this field with the application of high energy radiations available from synchroton [11-15]. In determining electronic structure of a solid, bonds and bands play important role and there is a strong correlation between these two entities. Like all other spectroscopic studies, X-ray spectroscopy also deals with ground state and excited state. Figure 1(a) depicts the correlation between X-ray spectra, chemical composition and ground state of the material, Similarly, Figure 1(b) shows the role of defects in studying the electronic properties.

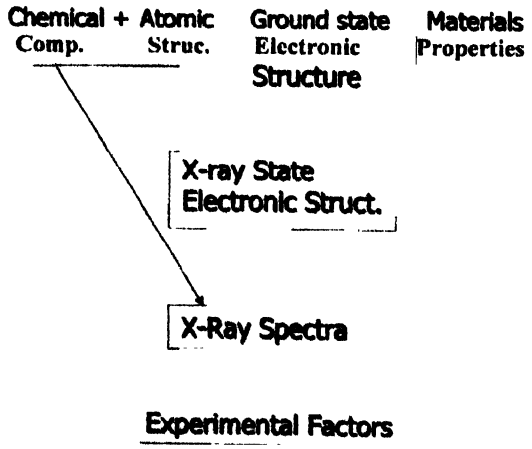

Figure 1(a). Relation between ground state electronic structure X-ray spectra and atomic structure.

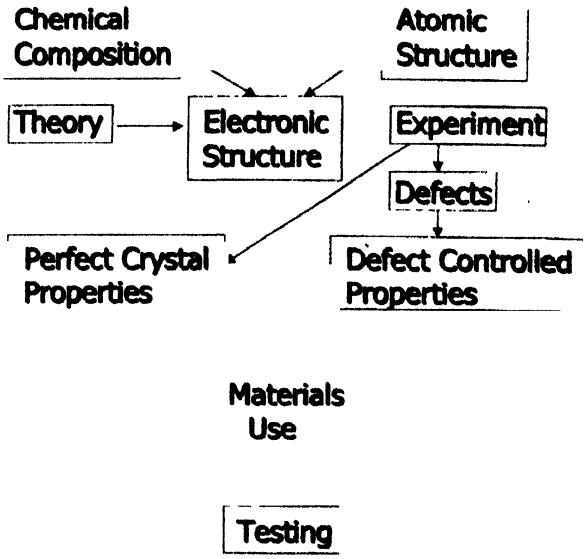

Figure 1(b). Role of structure and defects in materials.

While X-ray line spectra are suited for study of inner electron levels of atoms, valence band spectra are useful for study of bonding between atoms. Generally X-rays are useful for three aspects of materials characterisation.

(i) X-ray line spectra provide a means to measure elemental composition such as Energy Dispersive X-ray Fluorescence (EDXRF), Wavelength Dispersive X-ray Fluorescence (WDXRE) and Total reflection X-ray fluorescence (TXRF).

(ii) X-ray diffraction (XRD) is exclusively used for determination of structure, perfection and imperfaction in crystal lattice or powders.

(iii) Details of X-ray spectra like, X-ray photoelectron spectra (XPS), Auger electron spectra (AES), near edge X-ray absorption fine structure (NEXAFS), Extended X-ray fine edge structure (EXFS), Soft X-ray emission spectra (SXES) and resonant inelastic soft X-ray scattering (RIXS) provide information on bonding, valence state, charge associated with the cation or anion and density of states at the atom at a particular site.

While X-ray absorption and emission spectra are more common for studying the bonding effect, XPS and AES have also been used in recent past [17] for studying the bulk and surface properties. Valence band spectra directly reflect the energies of bonding electron while diagram line spectra provide an indirect measurement of valence electron distribution. Using XES it has been possible to determine the charge associated with cation in $3d$ transition metals like 'Mn' and hence to correlate the binding energy of $2p_{3/2}$ level with the no. of unpaired electrons in several Mn

compounds [16]. Accordingly localised states have been found to be present at the top of the valence band, by using soft X-ray emission spectra also. Since effective charges related to line shifts are real space ® integrals over electron density, X-ray spectra are given theoretically by integrals over momentum or *K* space or energy, electronic structure of compounds can be found out from soft X-ray emission study.

2. Alloy thin films

In alloy thin films of bismuth antimony sulphide the charge associated with sulphur ion has been found to agree with the theoretically calculated value [18]. Further, the satellite bands present in sulphur spectra reveal the presence of localised states present in such thin film system. Low energy satellites explain the hybridization of '*p*' orbital of '*s*' with *d* orbitals of cations.

Since soft X-ray emission spectra give the density of states (DOS) at the site of the emitting atoms, it has been observed that in Pb-Hg S thin films, the DOS at Fermilevel (E_f) decreases with alloying component [19]. Bonding parameters in such films have been calculated using the chemical shift of sulphur K_a line from the soft X-ray emission study [19]. The bonding has been found to be homopolar for PbS and the bonding parameter (*1*) decreases with the increase in Hg content becoming neutral at certain concentration and then increases to become homopolar for HgS.

3. Transition metals and super conductors

X-ray emission spectra not only reflect the unperturbed band structure but also the response of electrons to the creation of inner shell vacancies. For semiconductor or superconductor containing '3*d*' transition metals soft X-ray emission spectra can throw light on the multiple ionisation or core hole-electron interaction taking place in this system (1b). It is also possible to calculate the valence state of metal ion in such compounds. In high T_c superconductors like YBCO and LBCO the valence state of copper has been found to be greater than two [20,21]. In Ba Sr TiO_3 system, it has also been possible to indentify the hybridization of 4*p* states of titanium with the 2*p* states of oxygen. This hybridization result in a increase in vacancies which pushed up the Fermilevel E_f [22]. Similar studies of TiN_x system using soft X-ray emission spectra have been carried out by Beauprez *et al* [23] who have attributed the shift to be hybridization of N 2*p* and Ti 3*d* states.

Shape and asymmetry of the emission spectra provide a lot of information about the electronic density of states of the material. The strength of asymmetry is chiefly determined by the density and symmetry of *s*, *p*, *d* and other electronic states near the Fermi level (E_f) [24,25]. Local symmetry, nearest neighbour distances crystal structure as well as vacancies created during X-ray emission also affect the emission band structure and asymmetries [26]. Once the deviation from peak symmetry is confirmed, it is possible to deconvolute or fit the emission spectra with curve fit programme. Such fitting of emission spectra in V_2O_5–MoO_3 system have been carried out by us and it has been possible to explain the satellite emission peaks on both side of the main band on the basis of vacancy production and Coster-Kronig process taking place in the system. On the basis of skewed shape of the emission bands (*i.e.* the low asymmetry indices) it has been possible to say that delocalisation of density of states in '*d*' orbital of vanadium takes place as more and more molybdenum atom occupy nearest neighbour and next nearest neighbour position in V_2O_5 matrix [27].

4. Carbides, borides, nitrides and silicides

The carbides, borides, nitrides and silicides of transition and refactory metals have numerous physical and chemical characteristics which make them important for detailed characterisation. The metalloids have a profound influence on the electronic density of states in these compounds. Bonding in these materials are discussed in the light of interaction between '*d*' orbitals and '*p*' orbitals of metalloids. Soft X-ray emission studies in these systems have indicated the role of Coster-Kronig processes, multihole configuration and shake off satellites originating in these system [28]. Recently Stadler *et al* [29] have studied the electronic structure of tungsten boride system using soft X-ray emission spectroscopy. They have compared the boron 1*s* emission (*K* emission) to the *p*-projected partial density of states (*p*-PDOS) local to the boron atom and have found excellent agreement of experimental spectral with DOS calculated by linear muffin tin orbital (LTMO) method.

5. Adsorbates and catalytic reagents

Application of soft X-ray emission spectroscopy in the field of organic superconductors and characterising surface states of the absorbates have also grained importance during the last few years. Since charge transfer between adsorbate and the catalyst forms a part in rate determining step in catalytic processes, it becomes appropriate to study such catalysts under soft X-ray excitation [30–33]. A positive shift in the

emission band spectra indicates charge transfer from cation to anion and a negative shift implies to that of anion [34]. The valence electrons also considerably affect the decay probability of doubly ionised states [35]. Using these clues, we have successfully determined the bonding in aluminum silicon containing clay minerals to be covalent [30]. Such clays have now been widely studied for their catalytic activities.

With the advent of synchroton radiation, energy in the soft X-ray region has been utilised to study the resonant inelastic X-ray scattering emission from various solids liquids and gases [36]. It has ushered a new dimension to the soft X-ray emission spectroscopy to unravell the structure of amorphous or crystalline or broad band materials. Density functional theory (DFT) has been used to calculate the ground state electronic structure using Cluster description [37,38].

Acknowledgments

The author thanks his colleagues Rajeev, L D Pradhan and B B Nayak for their help in many soft X-ray emission spectra studies. Further, the author thanks the Director, RRL, Bhubaneswar for kind permission to publish the work.

References

[1] Edward A Stern and R W Siegel *Current Opinion in Solid St. and Mater. Sci.* **4** 321 (1999)

[2] R W Siegel, E Hu and Roco M C Roco (eds) *World Technology Evaluation Centre Panel Report on : Nano Structure Science and Technology* (Kluwer : Dordrecht) p 336 (1999)

[3] Y Yacoby and E A Stern *Comments on Condensed Matter Phys.* **18** 1 (1996)

[4] *J. Elect. Spectrosc. Related Phenom.* **110-111** (2000) Devoted to SXES

[5] B S Acharya, Rajeev, R Sakthivel and L D Pradhan *Indian J. Phys* **74A** 131 (2000)

[6] B S Acharya, Rajeev, L D Pradhan, P Mishra and B B Nayak *X-Ray Spectrometry* **29** 279 (2000)

[7] B S Acharya, Rajeev, L D Pradhan, B B Nakyak and P Mishra *Bull Mater. Sci.* **22** 981 (1981)

[8] B S Acharya and R Sakthivel *X-Ray Spectromet.* **23** 236 (1994)

[9] A Meisel, G Leonhardt and R Szargan (eds) *X-Ray Spectra and Chemical Binding* (Berlin : Springer Verlag) (1989)

[10] D S Urch in *Chemical Bonding and Spectroscopy in Mineral Chemistry* (eds) Berry F J and Vaughan D J (London : Chapman & Hall) **Chapter-II** (1985)

[11] S Eisebitt and Weberhardt *J. Electron Spectrosc. Rel. Phenom.* **110-111** 335 (2000)

[12] J Erik Rubensson *J. Electron Spectrosc. Rel. Phenom.* **110-111** 135 (2000)

[13] J Nordgren and J Guo *J. Electron Spectrosc. Rel. Phenom.* **110-111** 1 (2000)

[14] S Stadler, R P Winarski, J MmacLaren, D L Ederer, J VanEk, A Mocwes, M M Grush, T A Callcott and R C C Perera *J Electron Spectrosc. Rel. Phenom* **110-111** 75 (2000)

[15] J H Guo, W T Zheng, C Sathe, N Hellgren, A Agui, J E Surdgrena and J Nordgren *J. Electron Spectrosc. Rel. Phenom.* **101-103** 551 (1999)

[16] B S Acharya, Rajeev and L D Pradhan *Jpn. J. Appl. Phys* **29** 1278 (1990)

[17] D Briggs and M P Seah (eds) *Practical Surface Analysis* (New York · John Wiley) (1985)

[18] B B Nayak, B S Acharya and S K Singh *Thin Solid Films* **164** 75 (1988)

[19] B S Acharya, S K Singh and B B Nayak *Phys. State. Solid (b)* **153** 153 (1989)

[20] S K Singh, B B Nayak, B S Acharya, U Shyamprasad, R K Galgali and B C Mohanty *Bull Electrochem.* **5** 571 (1989)

[21] B S Acharya, Rajeev, J Muralidhar, L D Pradhan and B B Nayak in *Proc. Int. Conf. on Super Conductivity* (Bangalore, Jan 10–14) **286-292** (1990)

[22] B S Acharya, Rajeev and L D Pradhan *Jpn. J. Appl. Phys* **32** 72 (1993)

[23] E Beauprez, C F Haque, J M Mariot, F Tenyssandier, J Redbuger, P Markseteiner and P Weinberger *Phys. Rev.* **B34** 886 (1986)

[24] Z M Stadnik, J C Fuggle, T Miyazak and G Stroinu *Phys. Rev* **B35** 7400 (1987)

[25] G K Wertheim and P H Citron in *Photoemission in Solids* **Vol. 1** (eds) L Leuy and M Cardona (Berlin : Springer Verlag) (1989)

[26] J J Jia, T A Calcott, W L O'Brien, Q Y Dong, D R Muller, D L Edever, Z Tan and J I Budnick *Phys. Rev.* **B46** 4446 (1992)

[27] B S Acharya, Rajeev, L D Pradhan, P Mishra and B B Nayak *X-Ray Spectromet.* **29** 279 (2000)

[28] B S Acharya, L D Pradhan and Rajeev *Mineral Process Extract Met. Rev.* **22** 165 (2001)

[29] S Stadler, R P Winarshi, J M MacLaren, D L Ederer, J VanEk, A Mocwes, M M Grush, T A Calcott and R C C Perera *J. Electron Spectrosc. Rel. Phenom.* **110-111** 75 (2000)

[30] B S Acharya, Rajeev and L D Pradhan *Petrotech* (held at New Delhi) (2001)

[31] O Karis, A Nilsson, M Weiell, C Puglia, N Wassdahl and N Martensson *Phys. Rev. Lett.* **76** 11380 (1996)

[32] C Keller, M Stichler, G Comeli, F Esch, S Lizzit, W Wurth and D Menzel *Phys. Rev. Lett.* **80** 1744 (1998)

[33] C B Stagarescu, L C Duda, K E Smith, D K Seo, M H Whangbo, D Jerome, R C Haddon, J S Brooks, J Guo and J Nordgren *J Electron. Spectrosc. Rel. Phenom* **101-103** 539 (1999)

[34] A Meisel in *Advances in X-Ray Spectroscopy* (eds) C Bomelle and C Mande (Oxford : Pergamon) **Chapt-18** (1983)

[35] A Meisel, G Leonhardt and R Szargan *X-Ray Spectra and Chemical Binding* (Berlin : Springer Verlag) (1989)

[36] S Eisebitt and W Eberhardt *J Electron Spectrosc. Related Phenom* **110-111** 335 (2000)

[37] L Trignero, L G M Petterson and H Agren *Phys. Rev.* **B58** 8097 (1998)

[38] P Bennich, T Wiell, O Karis, M Meinelt, N Wassdahl, A Nilsson, M Nyberg, L G M Petterson, J Stohr and M Samant *Phys. Rev* **B57** 9274 (1998)